

Selective Bond Breaking in Amorphous Hydrogenated Silicon by Using Duke FEL

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ABSTRACT

In order to study the possibility of influencing the phase containing predominantly Si-H bonds, samples of a-Si were exposed to Duke-FEL Mark III radiation, which was selected to fit the maximum absorption of stretching vibrations of Si-H bonds. By varying the wavelength in the vicinity of $5\mu\text{m}$, the illumination time, and the power density, different types and degrees of structural ordering of Si-H bonds Si-Si bonds were obtained, and monitored by Raman spectroscopy. Using $5\mu\text{m}$ at 10 kW/cm^2 leads to increase in structural disordering. However, increasing power to 60 kW/cm^2 improves both short and intermediate order in a-Si:H. Further increasing power density by an order of magnitude results in crystallization of the sample.

1. INTRODUCTION

Hydrogen is of crucial importance for improvement of the electronic and optical properties of a-Si:H. It has been suggested that the degradation of a-Si:H by illumination, Stabler-Wronski effect (SW), may be also related to the role of hydrogen and its effects on the variations in the microscopic structure^{2,3,4}. Experiments suggest that the SW effect is not only related to local breaking of “weak” Si-Si bonds⁵, but also to changes beyond the short-range order (SRO, nearest neighbor^{6,7}). Thus, the role of the hydrogen in the determination of the network order, short range and in particular, intermediate-range order (IRO, beyond nearest-neighbor), become an important question. Structural changes and defect formations may be caused by photo induced breaking of a Si-Si bonds just behind Si-H bonds⁸.

2. EXPERIMENTAL AND RESULTS

In this work we report on the effect that the irradiation of a-Si:H sample at FEL frequency resonant with the Si-H bonds has on its SRO and IRO. We demonstrate that the direct excitation of the lattice vibration by an intense ultra short laser pulse with an appropriate wavelength can induce improvement of the SRO and IRO even at room temperature, without increasing the temperature of the sample. We used samples of a-Si:H, deposited by hot wire deposition at NREL on glass and mono crystalline Si substrate. The samples were exposed at the Duke FEL Mark III to the 4.7 to $5.2\mu\text{m}$ radiation. The Raman spectra were taken by double grating spectrometer supplied with water cooled photomultiplier. As a source for the 514.5 nm excitation beam, Ar ion laser was used.

As can be seen from Fig. 1 after irradiation with 10 kW/cm^2 the effect of the irradiation caused increase in the intermediate range disorder in the material. The ratio of the areas under TA peak and TO peak (the $I_{\text{TA}}/I_{\text{TO}}$ ratio) increased as a consequence of irradiation and the width of the TO vibration mode slightly increased. The TA peak (around 160 cm^{-1}) represent the IRO, and involves triads of atoms representing

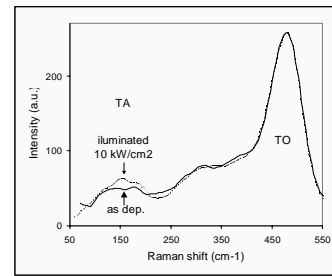


Fig.1. Raman spectra of as deposite a-Si:H sample (full line) and illuminated with $5\mu\text{m}$ and 10 kW/cm^2 (dashed line). Spectra are normalized to the same intensity of TO

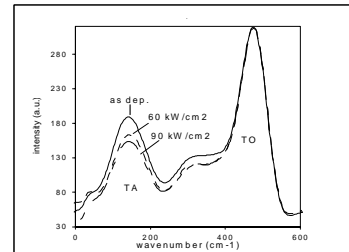


Fig 2. Raman spectra of Si-Si related part for as deposited sample (full line) and the 20 minutes irradiated sample with 60 (dotted line) and 90 kW/cm^2 (dashed line)

bond bending and the dihedral angle fluctuations. The transverse-optical (TO) vibration mode, peak (around 480 cm^{-1}) reflects the degree of the SRO and shows no change.

The changes in phonon related peaks are in close relations with changes in part of spectra related to Si-H stretching vibrations. In Fig.3 are plots of the spectra of as deposited sample (full line) and illuminated with 60 kW/cm^2 (dotted line) and 90 kW/cm^2 (dashed line)

while on Fig.2 are the corresponding spectra related to Si-Si bonds. As can be seen, the larger the surface under the Si-H stretching peak, the lower I_{TA}/I_{TO} ratio (the spectra are normalized to the I_{TO} peak and the TA peak in Fig. 2 is lower). It suggests that the increase in IRO is

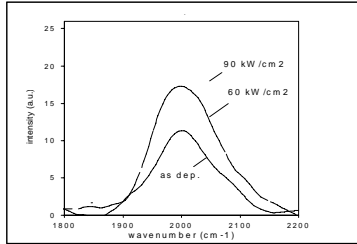


Fig.3 Raman spectra Si-H related part for as deposited sample (full line) and the irradiated sample with 60 (dotted line) and 90 kW/cm² (dashed line).

connected to increase in the number of Si-H bonds, which is proportional to the Si-H stretch mode peak.

We also explored the effect of wavelength on the IRO and SRO. Fig. 4 shows a spectra of as deposited sample (full line) illuminated for the same amount of time by the same power intensity (80 kW/cm²), but with different wavelengths (denoted on the graph). The spectra are normalized on the same peak value in order to illustrate the changes in the peak shape caused by illumination. It appears that only irradiation at the resonant wavelength of the Si-H bonds leads to a narrower peak.

Further increase of the irradiation intensity to the order of MW/cm² leads to the a-Si:H recrystallization. Figure 5. shows a sample of a-Si:H before and after irradiation. One can see that irradiation produces the peak, which is characteristic for the poly crystalline Si. The typical peak position of crystallized material was between 516 and 518 cm⁻¹.

SUMMARY

In summary, we demonstrated the possibility of changing Si-H bonding configuration with FEL IR radiation, without heating all of the sample volume. By proper choice of wavelength in the vicinity of 5 μ m, energy density and duration of illumination it is possible to increase the Si-H bonds ordering and in some extent to change the Si-H bonds concentration. This possibility enables to prove direct correlation between concentration of bonded hydrogen and intermediate and short range structural ordering.

Regarding the material modification, it can be concluded that the irradiation of a-Si samples with low intensity (about 10 kW/cm²) leads to decrease in the IRO of the material. Irradiation at intermediate intensity (100 kW/cm²) and with the resonant wavelength of the Si-H bonds increases both IRO, (I_{TA}/I_{TO} lower), and SRO (Γ_{TO} narrower), and also increases the local order in the material (Γ_{2000} narrower).

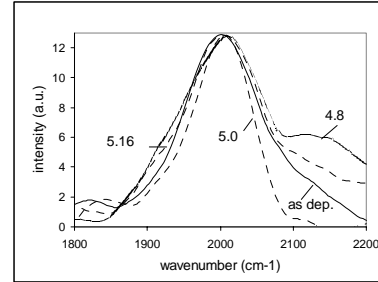


Fig.4 The spectra of as deposited a-Si:H sample (full line) and illuminated with same energy and time while different wavelengths (denoted in μ m on the graph).

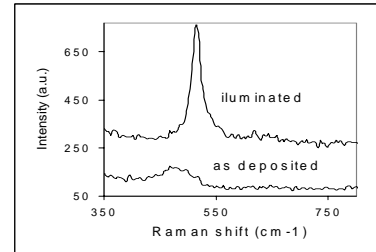


Fig.5. Raman spectra of as deposited a-Si:H sample and illuminated with $3 \cdot 10^3$ kW/cm² for 1 min.

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